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Enzymatic polymerization of biobased polyesters and polyamides

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Summary

Nowadays "green" is a hot topic almost everywhere, from retailers to universities to industries; and achieving green has become a universal perspective. However, polymers are commonly considered not to be “green”, being associated with massive energy consumption and severe pollution problems (e.g. the “Plastic Soup”) as a public stereotype. To achieve green polymers, three elements should be entailed:

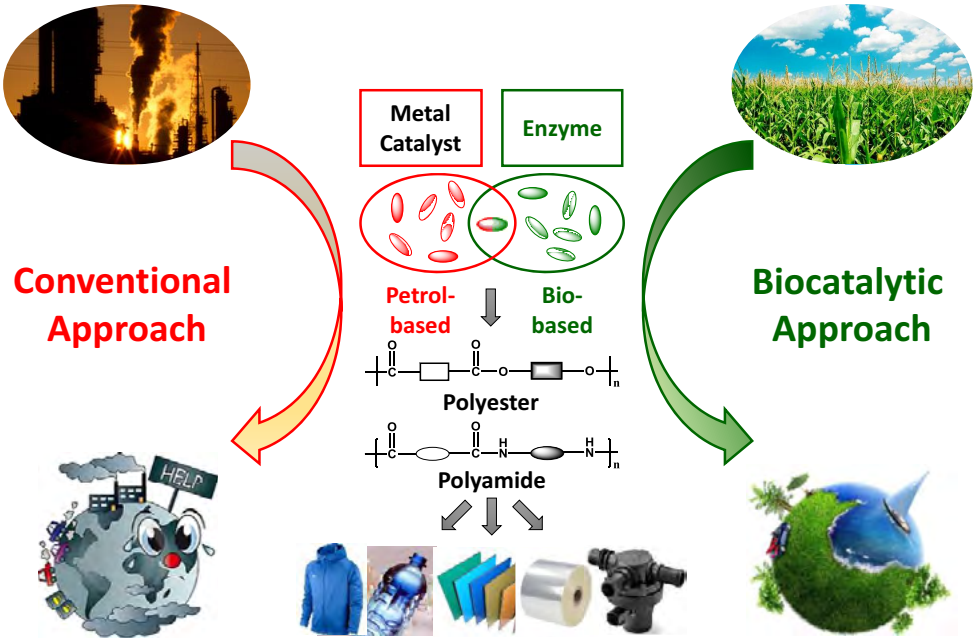
(1) green raw materials, catalysts and solvents;

(2) eco-friendly synthesis processes; and

(3) sustainable polymers with a low carbon footprint, for example, (bio)degradable polymers or polymers which can be recycled or have a low environmental impact upon disposal.

By utilizing biobased monomers in enzymatic polymerizations, many advantageous green aspects can be fulfilled (Scheme 1). For example, biobased monomers and enzyme catalysts are renewable materials which are derived from biomass feedstocks; enzymatic polymerizations are clean and energy saving processes; and no toxic residuals contaminate the final products. Therefore, synthesis of renewable polymers via enzymatic polymerizations of biobased monomers provides an opportunity for achieving green polymers and a future sustainable polymer industry, which will eventually play an essential role for realizing and maintaining a green and sustainable society.

In this research, we investigated the enzymatic polymerization of different combinations of (potential) biobased monomers under mild conditions, using Novozym® 435 (an immobilized form of *Candida antarctica* lipase b (CALB)) as the biocatalyst. The monomers used were aliphatic diacids and diesters, aliphatic diols and polyols, furan monomers and aliphatic diamines. Novozym® 435 was chosen over other lipases, as it possesses a broad substrate specificity, stable performance and tolerates diverse conditions. We succeeded in preparing various biobased polymers including saturated aliphatic polyesters, unsaturated aliphatic polyesters, furan polyesters and furan polyamides.



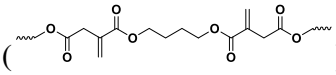
Scheme 1. Polymers go even greener: synthesis of biobased polyesters and polyamides via a biocatalytic approach - enzymatic polymerization of biobased monomers derived from renewable resources.

Aliphatic polyesters are (potential) biobased polymers which present many attractive attributes such as (bio)degradability, biocompatibility and possibly bioresorbability. We successfully synthesized a series of saturated aliphatic polyesters, poly(butylene dicarboxylate)s, via the enzymatic polymerization of 1,4-butanediol and diacid ethyl esters differing in chain length (n = 2, 3, 4, 6, 8 and 10 - number of methylene units in the diacid fragment), using a two-stage method in diphenyl ether at 80 °C (see **Chapter 4**). High molecular weight poly(butylene dicarboxylate)s were obtained, with $\overline{M_w}$'s of up to 94000 g/mol. We found that increasing the chain length of diacid ethyl ester from 2 to 4 resulted in poly(butylene dicarboxylate)s of significant higher molecular weights; however, upon further increasing the chain length from 4 to 10, poly(butylene dicarboxylate)s with lower molecular weights were obtained. Meanwhile, the enzymatic polymerization with diethyl succinate (n = 2) gave the lowest molecular weight products. This suggested that CALB prefers diacid ethyl esters having a chain length of more than 2 (n > 2); and CALB shows the highest specificity for diethyl adipate (n = 4) among the tested diacid ethyl esters.

Itaconate-based aliphatic polyesters are interesting biobased photo-curable polymers containing C=C bonds appended to the polymer main chain. Normally it is quite a

challenge to synthesize itaconate-based polyesters via conventional approaches, due to the low reactivity of itaconate and the occurrence of isomerization or cross-linking of the C=C bonds at elevated temperatures or by metal catalysts. However, we successfully prepared various high molecular weight itaconate-based unsaturated polyesters, poly(butylene dicarboxylate-*co*-itaconate)s, via the enzymatic polymerization of 1,4-buatnediol, dimethyl itaconate and diacid ethyl esters varying in chain length (**Chapters 2 - 4**).

We firstly investigated the effects of polymerization conditions on the two-stage enzymatic polymerization of diethyl succinate, itaconate and 1,4-butanediol in solution (**Chapter 2**). With the established method, poly(butylene succinate-*co*-itaconate)s (PBSIs) with $\overline{M_w}$'s of up to 22600 g/mol were produced via the enzymatic polymerization; however, a maximum of ~ 25 mol % of itaconate can be incorporated into the final products.

Subsequently we investigated the enzymatic synthesis of PBSI by using different monomer substrates, as well as, by applying different polymerization methods (**Chapter 3**). We found that the enzymatic polycondensation of succinic acid, itaconic acid, and 1,4-butanediol only yielded oligomers, with $\overline{M_w}$'s of around 500 - 1500 g/mol, despite different polymerization methods were used. By replacing the unactivated dicarboxylic acids with alkyl diesters, PBSIs with various molar compositions and significant higher molecular weights were obtained, with $\overline{M_w}$'s of up to 28300 g/mol. In addition, we found that the azeotropic polymerization in the mixture of cyclohexane and toluene is the most suitable approach for the synthesis of high molecular weight PBSIs with desirable chemical compositions; the two-stage enzymatic polymerization in diphenyl ether is capable of producing high molecular weight PBSIs with less than 30 mol % of itaconate; and the two-stage enzymatic melt polymerization gives PBSIs with controllable chemical compositions but low molecular weights. Moreover, the ^{13}C-NMR study revealed that different microstructures are present in PBSIs obtained from different polymerization methods. The formation of I-B-I-3 microstructures () is crucial for synthesizing high molecular weight PBSIs with desired chemical compositions; and CALB is capable of producing more I-B-I-3 microstructures in the mixture of cyclohexane and toluene by azeotropic distillation.

However, by replacing diethyl succinate (n = 2) with the other diacid ethyl esters with relatively longer chain length (n = 3 ~ 10), the two-stage enzymatic polymerization in diphenyl ether resulted in a series of unsaturated aliphatic polyesters with desired molar compositions and high $\overline{M_w}$'s of up to 57900 g/mol

(**Chapter 4**). The molar percentage of itaconate in the unsaturated polyesters can be tailored from 0 ~ 35 % by adjusting the feed ratio of itaconate; and all C=C bonds were well preserved in the resulting polyesters. We found that the enzymatic polymerization involving a higher feed ratio of itaconate generally gave lower molecular weight products; however, with diethyl dodecanedioate having the longest chain length (n = 10) among the tested diacid ethyl esters, higher molecular weight products were obtained at higher feed ratios of itaconate. Moreover, the obtained itaconate-based polyesters can be thermally cross-linked (**Chapter 3**) or photo-cured (**Chapter 4**). We found that the thermal and mechanical properties of the cross-linked polyesters can be controlled by adjusting the chain length of diacid ethyl ester units and the amount of itaconate units incorporated into the main chain.

From **Chapters 2 - 4** we can draw the conclusion that enzymatic polymerization is a versatile and powerful approach for the production of aliphatic polyesters and unsaturated aliphatic polyesters. However, the obtained aliphatic polymers possess low values of T_g ($\leq$ - 30 °C) and T_m ($\leq$ 115 °C). For applications needing polymers with higher T_g and T_m, we developed a robust biocatalytic approach towards semi-aromatic polymer analogues, furan polyesters and furan polyamides, with T_g of up to 120 °C and T_m of up to 160 °C. (**Chapters 5 - 7**).

We studied the enzymatic polymerization of 2,5-bis(hydroxymethyl)furan (BHMF) and various diacid ethyl esters, using the two-stage method in diphenyl ether at 80 °C (**Chapter 5**). BHMF-based polyesters with low molecular weights were produced ($\overline{M_w}$'s of around 1800 - 2900 g/mol). The polymerization kinetic study and MALDI-ToF MS analysis revealed that ether end groups were formed during the enzymatic polymerization, which led to the low molecular weights.

However, 2,5-furandicarboxylic acid (FDCA)-based furanic-aliphatic polyesters were successfully produced via the enzymatic polymerization of dimethyl FDCA with various aliphatic diols, using a temperature-varied two-stage method in diphenyl ether at 80 - 140 °C (**Chapter 6**). These FDCA-based furanic-aliphatic polyesters are sustainable alternatives to semi-aromatic polyesters and have great commercial interest as commodity polymers and thermoplastic engineering polymers. The obtained FDCA-based furanic-aliphatic polyesters reached a very high $\overline{M_w}$ of up to 100000 g/mol, which is normally hard to achieve by enzymatic polymerization. For the first time we demonstrated that enzymatic polymerizations are capable of producing high molecular weight FDCA-based polyesters, which have been primarily synthesized via step-growth polymerization using organometallic catalysts at elevated temperatures at around 150 - 280 °C. Moreover, we found that CALB prefers long-chain alkane-α,ω-aliphatic linear diols containing more than 3

carbons. Furthermore, the FDCA-based furanic-aliphatic polyesters possess similar crystalline and thermal properties compared to their petrol-based counterparts, semi-aromatic polyesters.

It is even more exciting that we successfully synthesized high molecular weight FDCA-based furanic-aliphatic polyamides from the enzymatic polymerization of dimethyl FDCA and 1,8-octanediamine, using a one-stage method in toluene at 60 - 100 °C or a temperature-varied two-stage method in diphenyl ether at 80 - 140 °C **(Chapter 7)**. The FDCA-based furanic-aliphatic polyamides can be used as a promising sustainable alternatives to petrol-based polyphthalamides (semi-aromatic polyamides) and be applied as thermoplastic engineering polymers and high performance materials. The enzymatic polymerization resulted in poly(octamethylene furanamide) (PA 8,F) with a very high $\overline{M_w}$ of up to 54000 g/mol. This is the first time that FDCA-based polyamides are successfully produced via enzymatic polymerization; and the molecular weights of the obtained PA 8,F are much higher than those produced via melt-polycondensation, the primarily synthesis approach for semi-aromatic polyamides, at elevated temperatures usually above 200 °C. Moreover, the obtained PA 8,F possesses a similar T_g and similar crystal structures, a comparable T_d, but a lower T_m, compared to its petrol-based counterpart, poly(octamethylene terephthalamide) (PA 8,T).

In addition, we established structure-properties relationships for the (novel) biobased polyesters by comparing crystalline/thermal properties of a series of relevant polymers. We found that the degree of crystallinity and T_m of the obtained aliphatic polyesters and BHMF-based polyesters generally increase with an increasing amount of methylene units incorporated into the polyester chains. This indicated that aliphatic polyesters and BHMF-based polyesters containing more methylene units possess higher crystallization ability. However, an opposite trend was observed for the synthesized FDCA-based furanic-aliphatic polyesters. Moreover, the T_g of the tested aliphatic polyesters and BHMF-based polyesters showed a parabolic trend towards the amount of methylene units in the polymer chains: the T_g firstly decreases with increasing amount of methylene units in the polyester chains; however, after the amount of methylene units reach a critical value, the T_g increases again. Regarding to the tested FDCA-based furanic-aliphatic polyesters, the T_g decreases with increasing amount of methylene units in the polymer chains. Furthermore, the amount of methylene units in the polyester chains showed no significant influence on the thermal stability of the tested polyesters with similar structures.

The synthesized biobased polyesters are promising sustainable alternatives to their petrol-based counterparts, which have broad potential applications (**Table 1**).

Table 1. Biobased polymers synthesized via enzymatic polymerizations in this research and their potential applications

Synthesized biobased polymers	Type of polymers	Target polymers to be replaced	Potential applications
A series of poly(butylene dicarboxylate)s including poly(butylene succinate)	Saturated aliphatic polyesters	Petrol-based aliphatic polyesters including poly(butylene succinate)	Commodity polymers Fibers Biomedical applications
Series of poly(butylene dicarboxylate-*co*-itaconate)s	Unsaturated aliphatic polyesters	Unsaturated aliphatic polyesters based on petrol-based unsaturated diacids	Thermosetting resins Biomedical applications Pharmaceutical applications
Poly(butylene furanoate)	Semi-aromatic polyester analogues	Poly(butylene terephthalate)	Commodity polymers Thermal engineering plastics
Poly(2,3-butylene furanoate)		Poly(2,3-butylene terephthalate)	
Poly(hexamethylene furanoate)		Poly(hexamethylene terephthalate)	
Poly(octamethylene furanoate)		Poly(octamethylene terephthalate)	
Poly(decamethylene furanoate)		Poly(decamethylene terephthalate)	
Poly(diethylene glycol furanoate)		Poly(diethylene glycol terephthalate)	
Poly(octamethylene furanamide)	Semi-aromatic polyamide	Poly(octamethylene terephthalamide)	Thermal engineering plastics High performance materials

The obtained saturated aliphatic polyesters can be used as commodity polymers and fibers, also in biomedical applications. For example, the synthesized fully biobased poly(butylene succinate) (PBS) can replace the current petrol-based PBS and partially biobased PBS, which is used as packaging material, mulch films, fiber and textile material, a matrix polymer or a modifier for composite materials, biodegradable drug encapsulation systems, and so on.

The obtained itaconate-based unsaturated polyesters can be used as replacement for other unsaturated polyesters based on petrol-based unsaturated diacids such as maleic, fumaric and glutaconic acids. These biobased unsaturated aliphatic polyesters can be applied as thermosetting resins for the manufacture of reinforced plastics and coatings, and have potential biomedical and pharmaceutical applications such as in sutures, bone screws, tissue engineering scaffolds and drug delivery systems.

The FDCA-based furanic-aliphatic polyesters can be used as sustainable substitutes to the current terephthalic acid (TPA) and isophthalic acid (IPA)-based semi-aromatic polyesters, which can be used as commodity polymers and thermal engineering plastics. For example, the obtained poly(butylene furanoate) (PBF) is a biobased alternative to poly(butylene terephthalate) (PBT), which has found broad applications in automotive industry (automotive exterior and interior parts, and auto electrical system components), electrical and electronics industries (for both signal and power uses), consumer goods (small handheld appliances and tools), cosmetics applications (leave-on, rinse-off and bath products), and so on.

The synthesized FDCA-based furanic-aliphatic polyamide, PA 8,F, is a green analogue to petrol-based PA 8,T, which can be applied as thermal engineering plastics and high performance materials in many industrial areas such as in automotive industry (add-on engine parts and in plastic-rubber composites), machinery and appliances industries (heavy metal replacement), electronic industry (LEDs and cable/wire protection), oil industry (gas pipes and supply lines), and so on.

Although we demonstrated in this research that enzymatic polymerizations are a powerful and green approach for the production of various biobased polyesters and polyamides, this approach also possesses some limitations and disadvantages:

(1) the atom efficiency is low as diesters were used at this stage of the research;

(2) non-ecofriendly solvents including diphenyl ether and toluene are used;

(3) long polymerization times are required for achieving high molecular weights;

(4) high reaction temperatures at around 100 - 140 ^{o}C were applied for enzymatic synthesis of polymers having a high T_m and low solubility; and the catalytic reactivity of enzymes decreases significantly at such elevated temperatures;

(5) the price of enzyme catalysts is still quite high;

(6) enzymatic polymerizations involving monomers with short chain length like 1,3-propanediol, monomers with secondary hydroxyl groups such as isosorbide and 2,3-butanediol, and polyols, result in low molecular weight products;

(7) the purify and price of biobased monomers remain a concern;

(8) last but certainly not least, only limited variety of biobased monomers are currently commercially available.

Therefore, more efforts are required to address these problems. For example, diacids can be used to improve the atom efficiency, green solvents such as ionic liquids and supercritical CO_2 can be employed as the reaction media, more robust and thermal stable enzymes should be developed for enzymatic polymerizations, improved and optimal processes should be explored for the production of diverse biobased monomers with high purity and low price, and so on.

At present, enzymatic polymerizations have already been poised for use in commercial process to prepare polymers targeted for cosmetic and medical applications. However, polymers including biobased polymers are still predominately produced via conventional approaches; and biobased polymers only represent a 2 % share of polymer production in 2013. However, due to the fast development of biotechnologies and enzymatic polymerization techniques, and the increased realization of the great benefits that enzymatic polymerizations and biobased monomers have to offer, there will be more highly value-added specialty biobased polymers produced commercially via biocatalytic approach in the near future. However, for the production of biobased commodity polymers, engineering plastics and high performance polymers, the commercial enzymatic process is promising but still has a long way to go, considering the high efficiency and low cost of the current pathways to the petrol-based counterparts.